

AD-A072 861

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY

F/G 10/2

PHOTOELECTROCHEMICAL CONVERSION OF OPTICAL ENERGY TO ELECTRICITY-ETC(U)

AUG 79 M S WRIGHTON

N00014-78-C-0630

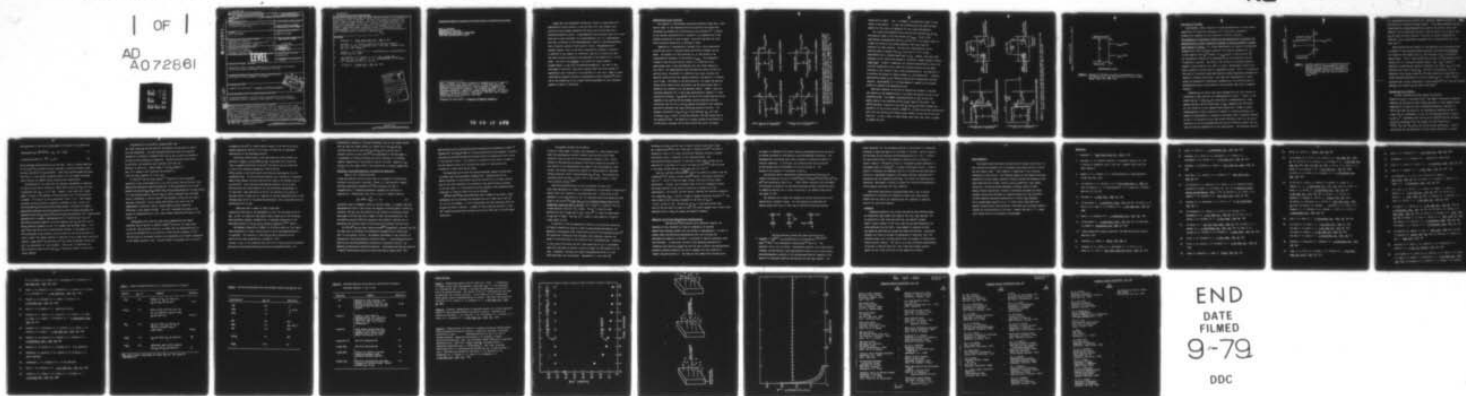
UNCLASSIFIED

TR-2-ONR

NL

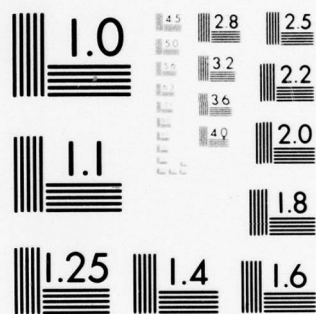
| OF |

AD  
A072861



END  
DATE  
FILMED  
9-79

DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

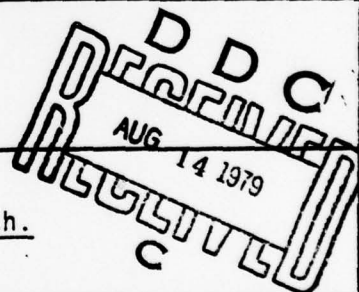
14 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
REPORT NUMBER TR-2-ONR	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photoelectrochemical Conversion of Optical Energy to Electricity and Fuels.		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report.
7. AUTHOR(s) Mark S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0630
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-696
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE Aug 14, 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 38
LEVEL		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States government; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared for publication in <u>Accounts of Chemical Research.</u>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoelectrochemistry, optical energy, semiconductor/liquid junction, photovoltaic effect, interfacial photochemistry, interfacial energetics		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Though the first documented photovoltaic effect is associated with a semi- conductor/liquid junction, it has not been until very recently that significant solar energy conversion efficiency could be realized with a photoelectrochemical device. A semiconductor/liquid junction solar cell is one where one or both electrodes in an electrochemical cell is a semiconductor such that irradiation of the semiconductor(s) results in the non-spontaneous flow of electric current in the external circuit. Photogeneration of storable chemical fuels in the form of electrolytic products is possible, in addition to the prospect of converting		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-014-6601UNCLASSIFIED 220 007 (over)  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A 072861

DDC FILE COPY



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

light only to electricity when the redox reaction occurring at one electrode is the reverse of that at the other. The aim of this report is to outline our recent research accomplishments in the field of photoelectrochemistry. Our work in this area began in late 1974 - more than a century after the first studies of photoeffects upon irradiation of an electrode in a cell and a number of years after modern pioneering studies of semiconductor/liquid interfaces which led to the formulation of our present working hypotheses of such interfaces exposed to optical illumination.

#### References

1. Becquerel, E. Compt. Rend. Acad. Sci., 1839, 9, 561.
2. Gerischer, H. in "Physical Chemistry: An Advanced Treatise", Vol. 9A, H. Eyring, D. Henderson, and W. Jost, eds., Academic Press: New York, 1970, Chapter 5.
3. Myamlin, V. A.; Pleskov, Yu. V. "Electrochemistry of Semiconductors", Plenum: New York, 1967.
4. (a) Brattain, W. H.; Garrett, C. G. B. Bell. System Tech. J., 1955, 34, 129; (b) Dewald, J. F. in "Semiconductors", N. B. Hannay, Ed., Reinhold: New York, pp. 727-752.
5. Williams, R. J. Chem. Phys., 1960, 32, 1505.

Accession For	
NTIS GPO&I	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	<input type="checkbox"/>
By _____	
Distribution/	
Availability Codes	
Dist	Availand/or special
A	-

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)



Photoelectrochemical Conversion of Optical Energy to Electricity and Fuels

Mark S. Wrighton  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

---

Mark S. Wrighton is currently Professor of Chemistry at M.I.T. where he began his career after receiving his Ph.D. in 1972 under the joint supervision of Professors Harry B. Gray and George S. Hammond at the California Institute of Technology. His research interests include photoelectrochemistry, catalysis, inorganic photochemistry, and surface chemistry. He was an Alfred P. Sloan Fellow, 1974-1976, and a Dreyfus Teacher-Scholar Grant recipient, 1975-1980.

---

[Prepared for publication in Accounts of Chemical Research.]

79 08 13 075

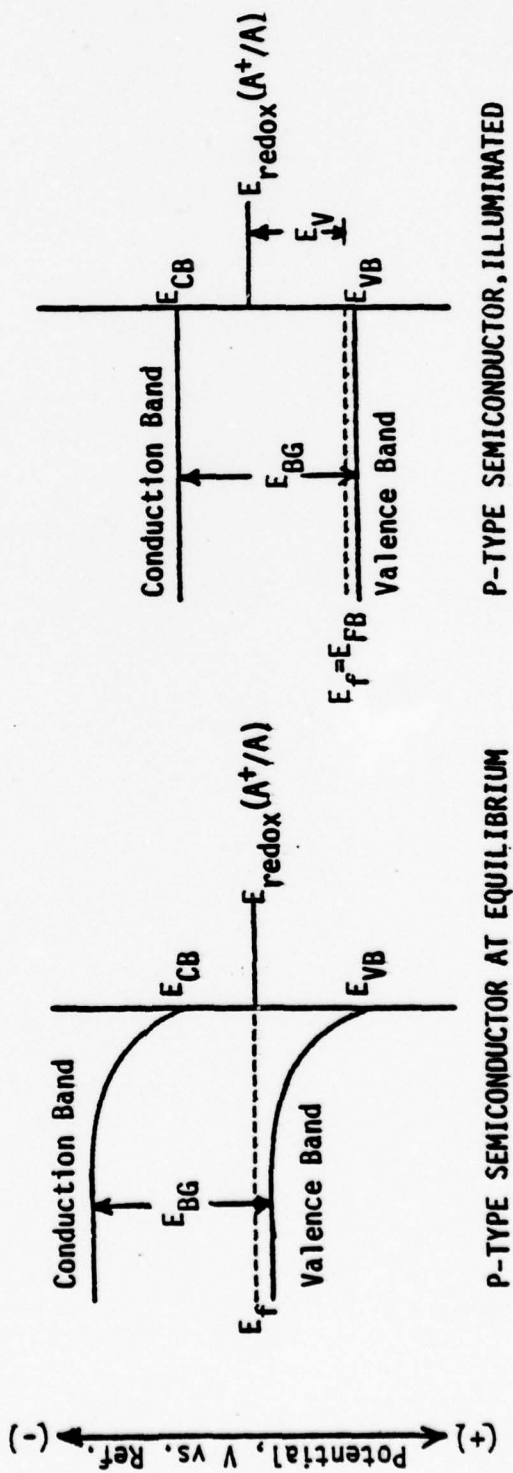
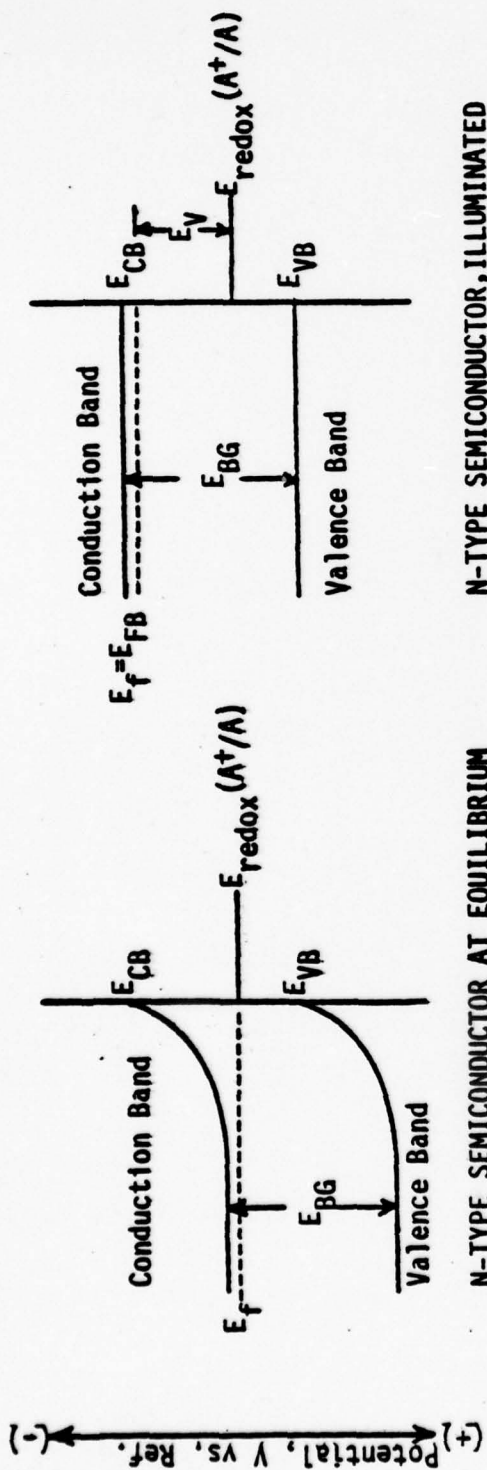
2

Though the first documented<sup>1</sup> photovoltaic effect is associated with a semiconductor/liquid junction, it has not been until very recently that significant solar energy conversion efficiency could be realized with a photoelectrochemical device. A semiconductor/liquid junction solar cell is one where one or both electrodes in an electrochemical cell is a semiconductor such that irradiation of the semiconductor(s) results in the non-spontaneous flow of electric current in the external circuit. Photogeneration of storable chemical fuels in the form of electrolytic products is possible, in addition to the prospect of converting light only to electricity when the redox reaction occurring at one electrode is the reverse of that at the other. The aim of this Account is to outline our recent research accomplishments in the field of photoelectrochemistry. Our work in this area began in late 1974 - more than a century after the first studies<sup>1</sup> of photoeffects upon irradiation of an electrode in a cell and a number of years after modern pioneering studies of semiconductor/liquid interfaces<sup>2-5</sup> which led to the formulation of our present working hypotheses of such interfaces exposed to optical illumination.

### Semiconductor/Liquid Junctions

Our research in semiconductor photoelectrochemistry began when a good working model for the semiconductor/liquid junction had already been formulated and perhaps best articulated by Heinz Gerischer.<sup>6a</sup> A summary of the junction characteristics is essential to an appreciation of the problems confronting us when we began. We briefly describe the interfacial situation essentially in Gerischer's terms.

Immersion of a semiconductor electrode into a liquid electrolyte solution may result in charge-transfer equilibration between the two media. The potential of the electrode,  $E_f$ , is then poised to the electrochemical potential of the solution,  $E_{\text{redox}}$ . The interesting finding is that the equilibration results in a relatively thick space-charge layer in the semiconductor near the surface exposed to the liquid. For semiconductors where the majority charge carriers are positive holes, the material is referred to as p-type, and where the majority charge carriers are negative electrons, the material is referred to as n-type. The effect of the equilibration is to reduce the majority charge carrier density near the surface, and the space-charge layer is therefore also referred to as the depletion region. Scheme I shows the interface energetics for n- and p-type semiconductors immersed in liquid electrolyte solutions.  $E_{\text{VB}}$  denotes the top of the valence band and can be regarded as the position of the highest occupied molecular orbitals delocalized over the solid, and  $E_{\text{CB}}$  denotes the bottom of the conduction band which represents the lowest unoccupied molecular orbitals. The energetic separation of  $E_{\text{VB}}$  and  $E_{\text{CB}}$  is the band gap,  $E_{\text{BG}}$ , and light of energy  $\geq E_{\text{BG}}$  is useful in exciting electrons from the valence band to the conduction band. The objective in energy conversion applications is to efficiently transduce the excited electron hole pairs to produce



**SCHEME I** Semiconductor/liquid junction energetics for an n-type semiconductor (top) and a p-type semiconductor (bottom) at charge transfer equilibrium (left) and under illumination at open circuit (right).  $E_{\text{redox}}$  denotes the Fermi level of the liquid and  $E_f$  the Fermi level of the semiconductor.  $E_{\text{FB}}$  is the so-called flat-band potential where the bands are not bent.



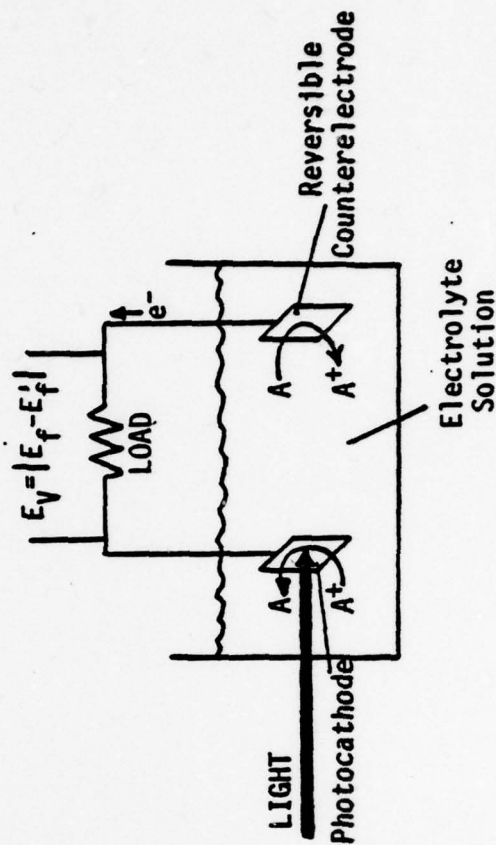
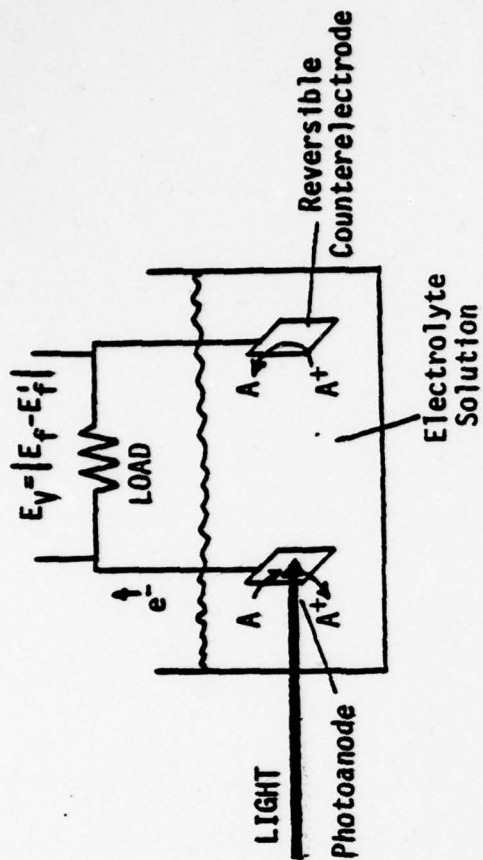
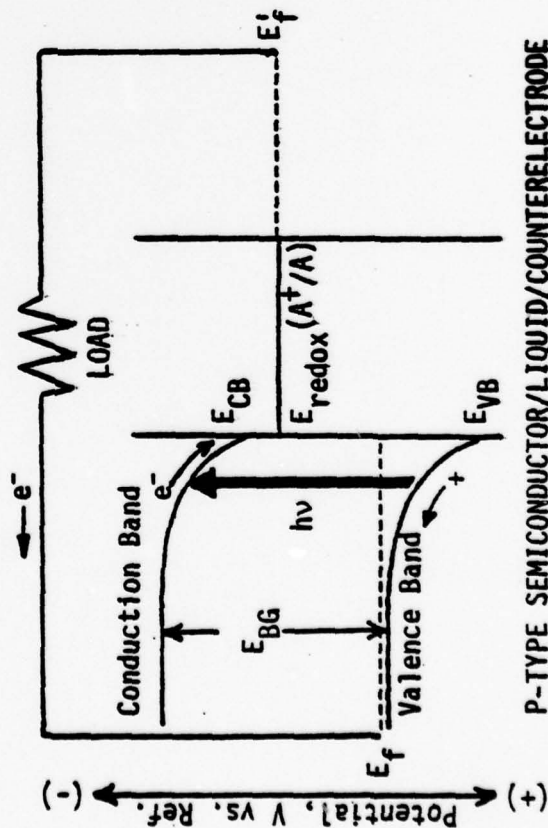
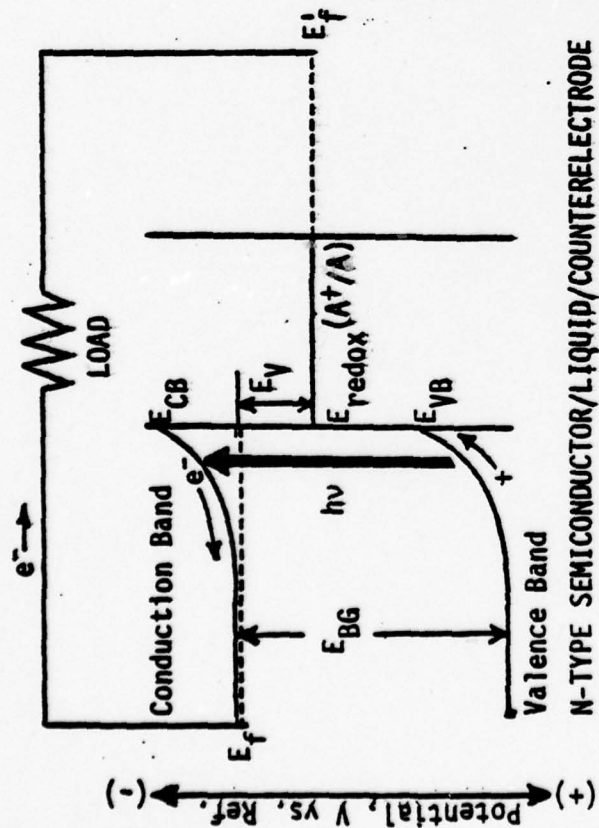
4

electricity or chemical fuel. In Scheme I, the depletion region is that region in the semiconductor near the interface where the bands are bent, upwards for the n-type and downwards for the p-type semiconductor.

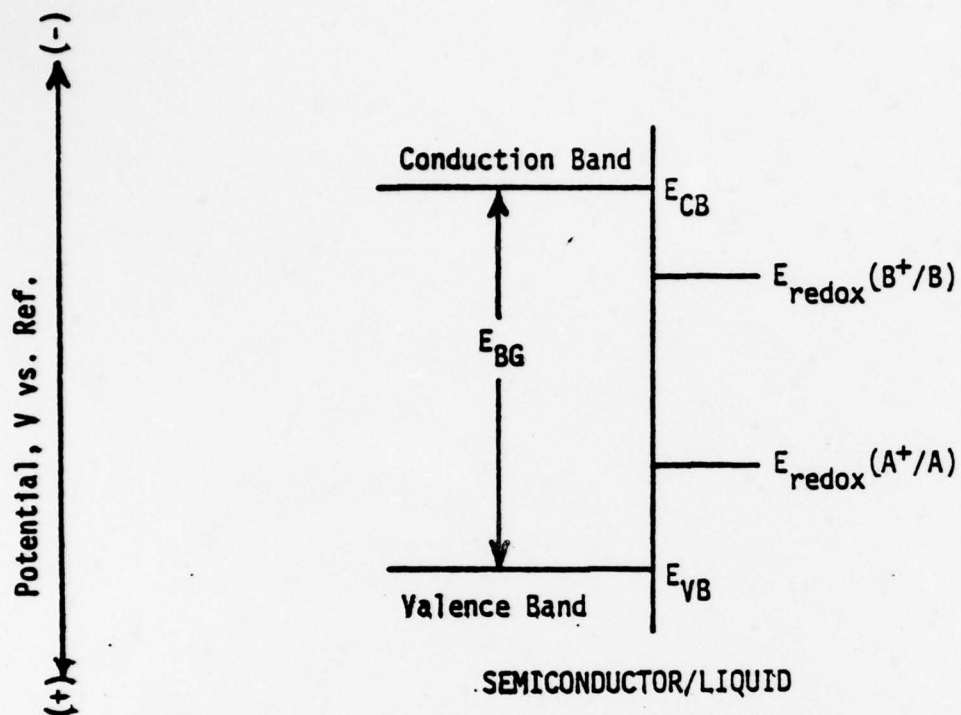
For a given semiconductor/liquid junction the positions  $E_{VB}$  and  $E_{CB}$  are generally taken to be fixed relative to  $E_{redox}$ . Owing to the band bending, photogenerated minority carriers ( $e^-$ 's for p-type, holes for n-type) are driven to the surface exposed to the liquid and are available for redox reaction. The hole for n-type materials has an oxidizing power no greater than  $E_{VB}$ , while the  $e^-$ 's for a p-type photocathode have a reducing power equal to  $E_{CB}$ . However, just what redox processes can be light driven depends on interfacial charge transfer kinetics (vide infra). Scheme II summarizes the interface energetics and circuits for so-called regenerative cells, where the reaction occurring at the photoelectrode is the reverse of that at the counterelectrode. The objective is to optimize the product of output voltage,  $E_V$ , and photocurrent. Increased band bending reduces  $E_V$  but inhibits electron-hole recombination and back reaction. Approximately 0.3 V of band bending is needed to give quantum yields for electron flow approaching unity.

When fuel formation in the form of electrolytic products is desired the reaction at the photoelectrode is not simply the reverse of that at the counterelectrode. For example, photoelectrolysis of  $H_2O$  involves the  $H_2O/H_2$  couple at one electrode and the  $O_2/H_2O$  couple at the other. The desired energetic situation is that the  $E_{CB}$  and  $E_{VB}$  positions straddle the potentials of the solution couples, Scheme III, so that the excited electron-hole pairs have the oxidizing and reducing power needed to drive the two half-cell reactions. In such a case, no other energy input other than light is needed to produce the fuel.





SCHEME II Full cell energetics, circuit and redox chemistry for n-type (top) and p-type (bottom) liquid junction cells for conversion of light to electricity.



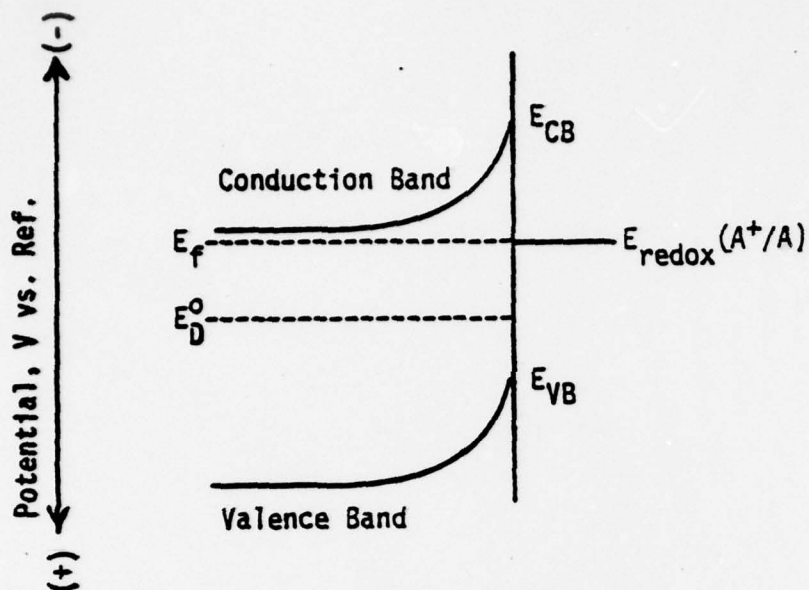
**SCHEME III** Energetics required to be able to photochemically drive the reduction of  $B^+$  and the oxidation of A with no other energy input other than light.

## The Practical Problems

Unfortunately, anodic reaction of n-type semiconductors is a hole process competitive with other hole processes, and in particular, photoanodic decomposition competes with the oxidation of solution reductants.

The consequence of photoanodic reaction of the semiconductor is disaster: the photoelectrode is either irreversibly consumed or surface corroded in a manner which renders it useless. All n-type semiconductors are subject to photoanodic decomposition, since the formal potential for oxidative decomposition,  $E_D^\circ$ , is more negative than  $E_{VB}^{7,8}$ . Further, if  $E_{redox}(A^+/A)$  is more positive than  $E_D^\circ$  spontaneous oxidation of the semiconductor by the electrolyte solution is possible in the dark. The rates of the various hole processes determine whether a given system will be inert; as always, thermodynamics reveals only what is possible, not the rate of a spontaneous process. But it is an empirical fact that all non-oxide n-type semiconductors undergo photoanodic decomposition reaction in aqueous electrolytes. Even some very thermodynamically robust oxides are susceptible to photoanodic decomposition; the oxidizing power of photogenerated holes in such materials can be greater than that of elemental fluorine.

Incorporating the notion that anodic decomposition can occur results in limitations to what junctions are thermodynamically stable. Further, to the extent that  $E_D^\circ$  is above  $E_{VB}$  one cannot obtain a thermodynamically stable junction having a barrier height equal to  $E_{BG}$ , suggesting that efficiency will be limited to a value somewhat below theoretical.<sup>7</sup> Scheme IV shows a thermodynamically stable junction with respect to oxidative processes, but whether the semiconductor is observed to be durable under illumination depends on the  $A \rightarrow A^+$  conversion having 100% current efficiency; that is, the rate of oxidation of A by the photogenerated hole must be infinitely greater than the rate of oxidative decomposition of the semiconductor. The sustained operation



**SCHEME IV** Interface energetics for a semiconductor/liquid junction which is thermodynamically stable to oxidative decomposition of the semiconductor; the semiconductor decomposition potential,  $E_D^0$ , is more positive than the solution potential,  $E_{redox}^{(A^+/A)}$ .



of a semiconductor/liquid junction cell, therefore, depends crucially on the kinetics of interfacial charge transfer. It has been speculated that all p-type materials undergo decomposition at least on the surface, simply upon immersion into an electrolyte solution, since the value of  $E_f$  at  $E_{FB}$  is near  $E_{VB}$  and there are holes available in the dark to provide a mechanism for oxidation.<sup>7</sup> Also, photocathodic decomposition of p-type materials may limit their use.<sup>7,8</sup>

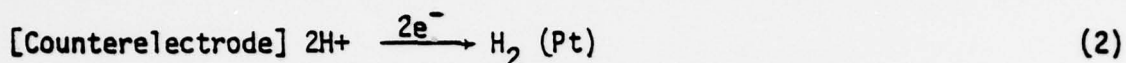
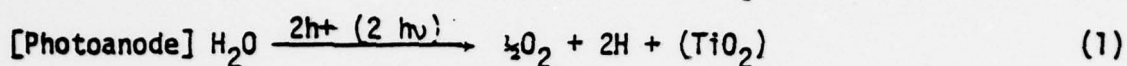
While maintaining the integrity of the photosensitive electrode surface is essential to any sustained energy conversion, the conversion efficiency will depend on the quantum yield,  $E_y$ , and the match of  $E_{BG}$  to the optical energy source. Like all other photovoltaic devices, the semiconductor/liquid junction cell is a threshold response system: light  $< E_{BG}$  in energy is completely transmitted and therefore ineffective, but light  $> E_{BG}$  is no more effective than light of energy  $E_{BG}$ . Sunlight is polychromatic, and the theoretical solar energy conversion efficiency maximizes at about 30% for a single photoelectrode-based cell with an optimum  $E_{BG}$  of  $\sim 1.4$  eV;<sup>9</sup> a double photoelectrode (p-type photocathode, n-type photoanode)<sup>6b</sup> cell with two different bandgaps could ideally be over 40% in efficiency!<sup>9</sup>

#### Photoelectrolysis of Water

In 1972, Fujishima and Honda claimed the sustained oxidation of  $H_2O$  at illuminated  $TiO_2$ .<sup>10</sup> Their paper; frustration at gasoline stations; and the desire to gain funding and entry in a new research field; stimulated us to begin our work in photoelectrochemistry, and early in 1975 we published the results of an investigation concerning the use of n-type  $TiO_2$  as a photoanode in a cell for the photoelectrolysis of  $H_2O$  to  $H_2$  and  $O_2$ .<sup>11</sup> Experiments were carried out in  $H_2O/D_2^{18}O$  solution and gases evolved at photoanode ( $TiO_2$ ) and cathode (Pt) were identified as  $^{18}O^{16}O$ ,  $^{16}O_2$ , and  $^{18}O_2$  and  $H_2$ , HD, and  $D_2$  by mass spectroscopy. Current efficiencies for the production of  $O_2$  and  $H_2$  were essentially in accord



with equations (1) and (2), and measurement of the mass of  $\text{TiO}_2$  before and



after prolonged photoelectrolysis was the same. Finally, current densities of  $\sim 0.5 \text{ A/cm}^2$  for  $\text{O}_2$  evolution were sustained in alkaline solution, using uv-laser excitation for  $\text{H}_2\text{O}$  oxidation. These data provided compelling proof that  $\text{TiO}_2$  is a very durable photoanode material for the highest sustained rate of optical to chemical energy conversion ever demonstrated.

But additionally, we found that the chemistry represented in equations (1) and (2) could not be effected by simply short-circuiting  $\text{TiO}_2$  to Pt and illuminating with  $>E_{\text{BG}} = 3.0 \text{ eV}$  light. Rather, it was found that a power supply in series in the external circuit providing  $\sim 0.2 \text{ V}$  of driving force is needed. The value of  $E_{\text{V}}$  for  $\text{O}_2$  evolution is only  $\sim 1.0 \text{ V}$ . Thus, though the water splitting requires a potential difference of only  $1.23 \text{ eV}$ , the  $3.0 \text{ eV}$  band gap  $\text{TiO}_2$  could not achieve this minimum voltage. The difficulty is readily appreciated from the fact that the  $\text{TiO}_2$  band positions relative to the  $\text{H}_2$  and  $\text{O}_2$  evolution potentials are such that  $E_{\text{CB}}$  is more positive than the  $\text{H}_2$  evolution potential by  $\sim 0.2 \text{ V}$ . Clearly, the photogenerated hole is capable (thermodynamically) of oxidizing  $\text{H}_2\text{O}$  to  $\text{O}_2$ , but the excited electron potential is not more negative than  $E_{\text{CB}}$  and falls shy of the  $\text{H}_2$  evolution potential by the  $\sim 0.2 \text{ V}$  needed from the power supply. It is very likely that short-circuit photocurrents observed in  $\text{TiO}_2$ -based cells in fact corresponds to  $\text{H}_2\text{O}$  oxidation to  $\text{O}_2$  but does not involve  $\text{H}_2$  evolution at the Pt; rather, the cathode reaction is reduction of  $\text{O}_2$  or some other electrolyte impurity. Indeed, Bard<sup>12</sup> has exploited the  $\text{TiO}_2$  system to generate electricity:  $\text{H}_2\text{O} \rightarrow \text{O}_2$  (photoanode)  $\text{O}_2 \rightarrow \text{H}_2\text{O}$  (cathode). Such a cell is inefficient for solar conversion owing to the large  $E_{\text{BG}}$  of  $\text{TiO}_2$  which results in only ultra-violet response.

8

TiO<sub>2</sub>-based cells as practical systems suffer from too large a band gap and the need for the external driving force in series with the photoeffect. The ideal photoelectrode would have the interface energetics as sketched in Scheme III where the O<sub>2</sub> and H<sub>2</sub> evolution potentials are the solution potentials of importance. Valence band holes would effect O<sub>2</sub> evolution, and conduction band electrons would have the potential to evolve H<sub>2</sub>. Excess energy in the E<sub>BG</sub> compared to the 1.23 V needed to split H<sub>2</sub>O would be necessary to drive the redox chemistry at a fast rate.

In 1976 we<sup>13</sup> and two other groups<sup>14,15</sup> reported the first sustained conversion of H<sub>2</sub>O stoichiometrically to H<sub>2</sub> and O<sub>2</sub> using light as the only input energy source, employing an n-type SrTiO<sub>3</sub>-based cell. For SrTiO<sub>3</sub> the short-circuit, full cell energetics are such that E<sub>CB</sub> and E<sub>VB</sub> straddle the H<sub>2</sub> and O<sub>2</sub> evolution potentials. Like TiO<sub>2</sub>, SrTiO<sub>3</sub> is a very durable material and was found to remain unchanged after prolonged use as a photoanode in alkaline media.<sup>13</sup> Unfortunately, SrTiO<sub>3</sub> has too large a band gap to be useful in solar energy applications, but such a cell has monochromatic ultraviolet light to stored chemical energy conversion efficiency in the range of 25-30%!. This still represents the state of the science in photoelectrolysis, with a solar energy conversion efficiency in the range of 1%.

SrTiO<sub>3</sub>-based cells have also been used to demonstrate the highest sustained rate of optical to chemical energy.<sup>16</sup> With an Ar ion laser tuned to the 351, 364 nm doublet emission, we showed that the photoelectrolysis of H<sub>2</sub>O can be effected with an O<sub>2</sub> evolution current density exceeding 5 A/cm<sup>2</sup>. The efficiency of the energy conversion was determined to be largely independent of the energy conversion rate. The data showed SrTiO<sub>3</sub>-based cells to be able

to generate  $>30 \text{ W/cm}^2$  of stored chemical energy in the form of  $\text{H}_2$  and  $\text{O}_2$  without substantial decline in efficiency and there was no detectable deterioration of the photoanode material.

Platinized single-crystal n-type semiconducting  $\text{SrTiO}_3$  effects the evolution of both  $\text{H}_2$  and  $\text{O}_2$  from  $\text{H}_2\text{O}$  when illuminated with ultraviolet light in aqueous electrolyte solutions.<sup>17</sup> The results are not surprising in view of the interface energetics; platinizing the  $\text{SrTiO}_3$  surface is not unlike short-circuiting the semiconductor to a Pt counterelectrode. For the platinized material  $\text{O}_2$  is evolved at illuminated, naked  $\text{SrTiO}_3$  whereas the platinized portions serve as the cathode (site of  $\text{H}_2$  evolution). Such platinized semiconductor material can be no more efficient than the electrochemical cell and suffers the disadvantages of (1) non-useful light absorption by the Pt, (2) evolution of  $\text{H}_2$  and  $\text{O}_2$  in the same region of space and (3) inability to run the photoelectrolysis at the "maximum power point" of the photocurrent/potential curve associated with the photoelectrolysis of  $\text{H}_2\text{O}$ .

There have been a number of other n-type semiconducting oxides used as the photoanode in a cell for the electrolysis of  $\text{H}_2\text{O}$ . So far, all materials used suffer from at least one of the following: poor wavelength response, decomposition, or improper disposition of the band edges relative to the  $\text{H}_2$  and  $\text{O}_2$  evolution potentials.<sup>18,19</sup> Table I.

The improper disposition of bands is a difficulty which at first would seem surmountable by simply varying the pH at which the photoelectrolysis is conducted. The rationale is that both  $\text{O}_2$  and  $\text{H}_2$  evolution are pH sensitive but always separated by a minimum of 1.23 V. The idea is that if the conduction band falls shy of the  $\text{H}_2$  evolution potential then the pH could be lowered to move the  $\text{H}_2$  evolution to a more positive value. For

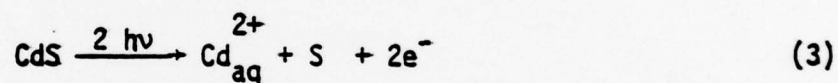


10

semiconductors generally, this may be possible, but for the oxides studied thus far they are either soluble at a useful pH or the  $E_{CB}$  and  $E_{VB}$  positions move with pH such that  $E_{CB}$  and  $E_{VB}$  and  $O_2$  and  $H_2$  are all constant relative to each other.<sup>20</sup> The pH dependence of the band edges is a consequence of surface acid-base equilibria resulting in a different chemical composition at the surface as the pH is varied. Generally,  $E_{VB}$  and  $E_{CB}$  will only remain fixed if the solution has a constant composition.

#### Non-Oxide, n-Type Semiconductors and Electricity Generation

There is not a single non-oxide, n-type semiconductor which has been shown to be capable of sustaining  $O_2$  evolution from  $H_2O$  when illuminated. Rather, all such materials undergo efficient photoanodic decomposition.<sup>7,8</sup> The situation with CdS is representative; it undergoes photoanodic decomposition according to equation (3). Photocurrent lasts only as long as it takes to form an



insulating layer of elemental sulfur on the CdS surface. It appears that the photogenerated holes in CdS do have the necessary oxidizing power to effect  $O_2$  evolution from  $H_2O$ , but the oxidation of the lattice is kinetically faster. Such seems to be the case with a number of other non-oxide materials, and our efforts since mid-1976 have focused on the problem of learning how to manipulate the relative rates of the various hole processes that may occur.

In 1976 we<sup>21</sup> and two other research groups<sup>22,23</sup> independently reported that CdS and CdSe could be protected from photoanodic decomposition by adding  $Na_2S$  and S to the aqueous solution. The dramatic improvement in the constancy of photocurrent from a CdSe-based cell is evident in Figure 1. In this system the oxidation reaction occurring at the photoanode is the oxidation of some polysulfide  $S_n^{2-}$ , and apparently not the oxidation of the lattice selenide. At the counterelectrode the reduction of some  $S_n^{2-}$  species obtains to give a cell where no net chemical change results. The

redox processes occurring at the two electrodes are the reverse of one another as in Bard's<sup>12</sup>  $\text{TiO}_2$ -based cell, but the  $E_{\text{BG}}$  for CdSe is 1.7 eV, giving significant visible response. Such cells thus can be used to sustain the conversion of light to electricity by putting a load in series in the external circuit. The situation is essentially that shown in Scheme II, and the objective would be to optimize the product of photocurrent and voltage for a given input optical power.

The sustained use of other non-oxide photoanodes depends on being able to protect them from photoanodic decomposition. Accomplishing this by adding reductants to the solution sacrifices the ability to directly oxidize  $\text{H}_2\text{O}$  (or any other reductant) but oxidation of the additive may be valuable in its own right, or if the oxidation can be reversed at the counterelectrode conversion of light to electricity can be effected.

We<sup>24</sup> and others<sup>25</sup> have now established that a number of non-oxide, n-type photoanodes can be protected from decomposition by at least one of the  $\text{X}_n^{2-}$  ( $\text{X} = \text{S}, \text{Se}, \text{Te}$ ) systems. A list of photoanodes and their band gaps which can be used are given in Table II. A number of these electrode materials in the  $\text{X}_n^{2-}$  containing electrolyte solutions yield fairly efficient ( $> 5\%$  efficiency) solar cells.



Non-aqueous solvents can be used to dissolve a large number of organic and organometallic redox couples which have fast heterogeneous electron transfer rates and which have formal potentials covering much of the electrochemical potential scale. Bard's studies of semiconductor/non-aqueous electrolyte systems has provided for the location of the semiconductor band edges on the electrochemical scale. Further, the studies revealed the presence of electrochemically important surface electronic levels situated between  $E_{VB}$  and  $E_{CB}$ . Such surface and interface states may play a crucial role in the overall kinetics in many liquid junction devices.<sup>26,27</sup>

Bard and Wrighton<sup>7</sup> pointed out that non-aqueous solvents could offer some advantage with respect to thermodynamics for photoanodic decomposition. Shortly after this assertion it was determined that  $I^-$  could serve as the reductant in an n-type CdS-based cell for sustained electricity generation when  $CH_3CN$  is the solvent.<sup>28</sup> In  $H_2O$ , the  $I_2$  or  $I_3^-$  oxidation product from  $I^-$  will oxidatively react with CdS in the dark, but in  $CH_3CN$  it is apparent that  $E_D^\circ$  is more positive than the  $I^-/I_3^-$  couple. The  $E_D^\circ$  is certainly more positive for CdS in  $CH_3CN$  than in  $H_2O$ , since  $Cd^{2+}$  is likely solvated better in  $H_2O$  than in  $CH_3CN$ . That the  $I_3^-/I^-$  couple is more negative in  $CH_3CN$  is likely useful as well.

In the Fall of 1977 we reported our results on the sustained conversion of light to electricity using an n-type Si-based photoelectrochemical cell employing a non-aqueous, EtOH, electrolyte solution of ferricenium/ferrocene.<sup>29</sup> The significant finding was that ferrocene could completely suppress the growth of insulating  $SiO_x$  on the surface of the Si photoelectrode. Formation of  $SiO_x$  occurs efficiently and even trace quantities of  $H_2O$  in non-aqueous media are sufficient to provide a source of oxygen for the formation of the  $SiO_x$ . Presumably, ferrocene can capture photogenerated holes at a rate which precludes such oxide growth. Subsequently, it was found that

13

ferrocene solutions could be used to obtain constant output from n-type Ge in EtOH-solution<sup>30</sup> and from n-type GaAs in CH<sub>3</sub>CN solution.<sup>27d</sup> Ferrocene is attractive, since it is a fast, one-electron reductant yielding a product, ferricenium, which is reducible at the counterelectrode. The ferricenium/ferrocene potential is such that a good output voltage can be obtained for n-type GaAs or Si (>0.5 V at open-circuit).<sup>27d,29</sup> n-Type Ge yields a low output voltage and has a small band gap (~0.7 eV).<sup>30</sup>

Thus far, the best efficiency<sup>(~12%)</sup> for electricity generation remains with the n-GaAs/Se<sub>2</sub><sup>2-</sup>/Se<sup>2-</sup> aqueous solvent system.<sup>25d</sup> However, non-aqueous electrolyte cells of 1 - 5% will likely be common without significant efforts toward optimization. Further, the non-aqueous media allow for fundamental studies not always possible in H<sub>2</sub>O owing to solubility or durability of the semiconductor. For example, we have recently examined the interface energetics for n-type MoS<sub>2</sub> (E<sub>BG</sub> = 1.75 eV) in CH<sub>3</sub>CN or C<sub>2</sub>H<sub>5</sub>OH electrolyte solutions.<sup>31</sup> The data allowed a very accurate assignment of the value of E<sub>FB</sub> at + 0.30 V ± 0.05 vs. SCE. The position of E<sub>VB</sub> is even more positive than that for CdS and about the same as TiO<sub>2</sub>.<sup>27</sup> This result suggests that visible light generated holes in MoS<sub>2</sub> are indeed very powerful oxidants.

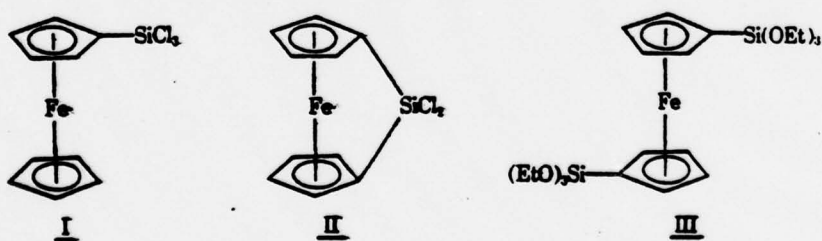
#### Chemically Derivatized Semiconductor Photoelectrodes

The discovery<sup>29</sup> that ferrocene could completely suppress the formation of SiO<sub>x</sub> formation on n-type Si prompted us to consider immobilizing ferrocene centers onto the surface of semiconductors, in order to protect them from destructive photoreaction while also allowing the photosensitive material to be useful in oxidizing or reducing substances other than ferrocene. In particular, we had in mind designing photosensitive interfaces which would be rugged and could be used to effect contrathermodynamic oxidation reaction ordinarily too slow to compete with SiO<sub>x</sub> formation at "naked" (non-derivatized) Si. The hope was that immobilized ferrocene would

be capable of completely efficiently capturing photogenerated holes and would be thereby converted to ferricenium at contrathermodynamic potentials. The photogenerated ferricenium would then be capable of effecting oxidation of solution reductants. In principle, any substance which can be oxidized by ferricenium would be oxidizable with the derivatized Si. The essence of the concept is illustrated in Figure 2.

The exciting idea of semiconductor photoelectrode derivatization was further stimulated by the work of Anson,<sup>32</sup> Hubbard,<sup>33</sup> Kuwana,<sup>34</sup> Miller,<sup>35</sup> Murray,<sup>36</sup> and Osa,<sup>37</sup> which was becoming known to us. Their efforts concerning the confinement of electroactive materials to reversible electrode surfaces provided the point of immediate departure for a flurry of activity in my research group during the summer of 1977.

Our approach was to adopt the procedure of surface derivatization using hydrolytically unstable silanes. For this purpose we synthesized the species I-III which have all been used to derivatize electrode surfaces.



Various electrode surfaces have been derivatized with reagents I - III<sup>38-49</sup> and characterized by electrochemical,<sup>38-40,43-45</sup> Auger,<sup>42</sup> XPES,<sup>41</sup> and photoacoustic spectroscopy,<sup>50</sup> Table III. The essential results are as follows. Electroactive material can be persistently attached, and derivatized n-type semiconductors generally give light-induced contrathermodynamic oxidation of the surface-bound material compared to the behavior of reversible materials derivatized with the same reagents. The

formal potential,  $E^\circ$ , for ferrocene confined to the surface of a reversible electrode is about the same as for ferrocene in solution. But on n-type Si, the ferrocene can be oxidized contrathermodynamically by  $\sim 0.5$  V. Further, for derivatized n-type Si the sequence of events occurs as sketched in Figure 2 where B = ferrocene or N,N,N',N'-tetramethyl-p-phenylenediamine in non-aqueous media or  $[\text{Fe}(\text{CN})_6]^{4-}$  in aqueous electrolyte solution. Finally, Figure 3 illustrates the remarkable ability of the derivatized electrode to survive as a photoanode compared to the naked electrode; apparently derivatization does not compromise efficiency for electricity generation, but substantial improvement in durability obtains by inhibiting photogenerated hole processes associated with  $\text{SiO}_x$  formation.

Derivatized semiconductor photoelectrodes offer a way to design photosensitive interfaces for effecting virtually any redox process. Efforts here are really just beginning and will comprise an important part of our continuing research.

### Prognosis

Photoelectrochemistry has already provided the most efficient means of transducing solar energy into chemical fuel ( $\text{H}_2 + \frac{1}{2}\text{O}_2$  from  $\text{H}_2\text{O}$ ,  $\sim 1\%$ ) or electricity ( $\sim 12\%$ ) using man-contrived, wet-chemical systems. There is great interest in this area; many new and good researchers are being attracted into the field. Large numbers of research articles are appearing reporting new systems and higher efficiencies. Significant advances are likely to be made in preparation of large area, thin film photoelectrodes, and in surface modification for purposes of manipulating charge transfer kinetics. The race is on to gain sufficient understanding to provide a scientific base for a new, large scale energy resource option for use in the first half of the twenty-first century.



### Acknowledgments

The research described above has been possible through the efforts of a very talented and energetic set of colleagues associated with M.S.W. during the last several years. Their research is summarized in the individual references to this article. The different aspects of the research have been supported by various Federal agencies including the National Aeronautics and Space Administration (oxides, direct  $H_2$  and  $O_2$  generation, laser energy conversion); the United States Department of Energy, Office of Basic Energy Sciences (exploratory interfacial photoredox processes for energy storage, derivatized electrodes for improved durability); and the Office of Naval Research (molecular manipulation of surface state energies). M.S.W. acknowledges support as an A. P. Sloan Fellow (1974-1976) and a Dreyfus Teacher-Scholar Grant Recipient (1975-1980) which provided financial flexibility during portions of this work. Support from the M. I. T. Cabot Solar Energy Fund is also gratefully acknowledged.



## References

1. Becquerel, E. Compt. Rend. Acad. Sci., 1839, 9, 561.
2. Gerischer, H. in "Physical Chemistry: An Advanced Treatise", Vol. 9A, H. Eyring, D. Henderson, and W. Jost, eds., Academic Press, New York, 1970, Chapter 5.
3. Myamlin, V. A.; Pleskov, Yu. V. "Electrochemistry of Semiconductors", Plenum, New York, 1967.
4. (a) Brattain, W. H.; Garrett, C. G. B. Bell System Tech. J., 1955, 34, 129; (b) Dewald, J. F. in "Semiconductors", N. B. Hannay, Ed., Reinhold, New York, pp. 727-752.
5. Williams, R. J. Chem. Phys., 1960, 32, 1505.
6. (a) Gerischer, H. J. Electroanal. Chem., 1975, 68, 263; (b) Bolts, J. M.; Ellis, A. B.; Legg, K. D.; Wrighton, M. S. J. Am. Chem. Soc., 1977, 99, 4826.
7. Bard, A. J.; Wrighton, M. S. J. Electrochem. Soc., 1977, 124, 1706.
8. (a) Gerischer, H. J. Electroanal. Chem., 1977, 82, 133; (b) Gerischer, H.; Mindt, W. Electrochim. Acta, 1968, 13, 1329.
9. "Solar Photovoltaic Energy Conversion", The American Physical Society, New York, 1979.
10. Fujishima, A.; Honda, K. Nature, 1972, 238, 37.
11. Wrighton, M. S.; Ginley, D. S.; Wolczanski, P. T.; Ellis, A. B.; Morse, D. L.; Linz, A. Proc. Natl. Acad. Sci. U.S.A., 1975, 72, 1518.

12. Laser, D.; Bard, A. J. J. Electrochem. Soc., 1975, 123, 1027.
13. Wrighton, M. S.; Ellis, A. B.; Wolczanski, P. T.; Morse, D. L.; Abrahamson, H. B.; Ginley, D. S. J. Am. Chem. Soc., 1976, 98, 2774.
14. Watanabe, T.; Fujishima, A.; Honda, K. Bull. Chem. Soc. Japan, 1976, 49, 355.
15. Mavroides, J. G.; Kafalas, J. A.; Kolesar, D. F. Appl. Phys. Lett., 1976, 28, 241.
16. (a) Wrighton, M. S.; Bocarsly, A. B.; Bolts, J. M. in "Radiation Energy Conversion in Space", K. W. Billman, ed., Vol. 61 of Progress in Astro-nautics and Aeronautics, 1978, p. 613; (b) Bocarsly, A. B.; Bolts, J. M.; Cummins, P. G.; Wrighton, M. S. Appl. Phys. Lett., 1977, 31, 568.
17. Wrighton, M. S.; Wolczanski, P. T.; Ellis, A. B. J. Sol. State Chem., 1977, 22, 17.
18. (a) Wrighton, M. S.; Morse, D. L.; Ellis, A. B.; Ginley, D. S.; Abrahamson, H. B. J. Am. Chem. Soc., 1976, 98, 44; (b) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. J. Phys. Chem., 1976, 80, 1325.
19. (a) Nozik, A. J. Ann. Rev. Phys. Chem., 1978, 29, 180; (b) Bard, A. J.; Hardee, K. L. J. Electrochem. Soc., 1977, 124, 215; (c) Kung, H. H., Jarrett, H. S.; Sleight, A. W.; Ferretti, A. J. Appl. Phys., 1977, 48, 2463.
20. Bolts, J. M.; Wrighton, M. S. J. Phys. Chem., 1976, 80, 2641.
21. Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc., 1976, 98, 1635.
22. Hodes, G.; Manassen, J.; Cahen, D. Nature, 1976, 261, 403.

23. Miller, B.; Heller, A. Nature, 1976, 262, 680.
24. (a) Wrighton, M. S.; Ellis, A. B.; Kaiser, S. W. Adv. Chem. Ser., 1977, 63, 71; (b) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc., 1976, 98, 6418, 6855, and 1977, 99, 2839; (c) Ellis, A. B.; Bolts, J. M.; Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc., 1977, 99, 2848; (d) Ellis, A. B.; Bolts, J. M.; Wrighton, M. S. J. Electrochem. Soc., 1977, 124, 1603.
25. (a) Miller, B.; Heller, A.; Robbins, M.; Menezes, S.; Chang, K. C.; Thomson, Jr., J. J. Electrochem. Soc., 1977, 124, 1019; (b) Heller, A.; Chang, K. C.; Miller, B. J. Electrochem. Soc., 1977, 124, 697; J. Am. Chem. Soc., 1978, 100, 684; (c) Chang, K. C.; Heller, A.; Schwartz, B.; Menezes, S.; Miller, B. Science, 1977, 196, 1097; (d) Heller, A.; Parkinson, B. A.; Miller, B. Appl. Phys. Lett., 1978, 33, 5121; (e) Robbins, M.; Bachman, .; Lambrecht, V. G.; Thiel, F. A.; Thomson, Jr., J.; Vadinsky, R. G.; Menezes, S.; Heller, A.; Miller, B. J. Electrochem. Soc., 1978, 125, 831.
26. Kohl, P. A.; Bard, A. J. J. Electrochem. Soc., 1979, 126, 598, 603.
27. (a) Frank, S. N.; Bard, A. J. J. Am. Chem. Soc., 1975, 97, 7427; (b) Kohl, P. A.; Bard, A. J. J. Am. Chem. Soc., 1977, 99, 7531; (c) Laser, D.; Bard, A. J. J. Am. Chem. Soc., 1976, 80, 459; (d) Kohl, P. A.; Bard, A. J. J. Electrochem. Soc., 1979, 126, 59.
28. Nakatani, K.; Matsudaira, S.; Tsubomura, H. J. Electrochem. Soc., 1978, 125, 406.
29. Legg, K. D.; Ellis, A. B.; Bolts, J. M.; Wrighton, M. S. Proc. Natl. Acad. Sci. U.S.A., 1977, 74, 4116.

30. Bolts, J. M.; Wrighton, M. S. J. Am. Chem. Soc., 1978, 100, 5257.
31. Schneemeyer, L. F.; Wrighton, M. S. submitted for publication.
32. Brown, A. P.; Koval, C.; Anson, F. C. J. Electroanal. Chem., 1976, 72, 379.
33. Lane, R. F.; Hubbard, A. T. J. Phys. Chem., 1973, 77, 1401, 1411.
34. (a) Armstrong, N. R.; Lin, A. W.; Fujihira, M.; Kuwana, T. Anal. Chem., 1976, 48, 741; (b) Evans, J. F.; Kuwana, T.; Henne, M. T.; Royer, G. P. J. Electroanal. Chem., 1977, 80, 409.
35. (a) Firth, B. E.; Miller, L. L.; Mitani, M.; Rogers, T.; Lennox, J.; Murray, R. W. J. Am. Chem. Soc., 1976, 98, 8271; (b) Firth, B. E.; Miller, L. L. ibid., 1976, 98, 8273; (c) Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. J. Am. Chem. Soc., 1975, 97, 3549.
36. (a) Moses, P. R.; Murray, R. W. J. Am. Chem. Soc., 1976, 98, 7435 and J. Electroanal. Chem., 1977, 77, 393; (b) Elliott, C. M.; Murray, R. W. Anal. Chem., 1976, 48, 1247; (c) David, D. G.; Murray, R. W. ibid., 1977, 40, 194; (d) Moses, P. R.; Wier, L.; Murray, R. W. ibid., 1975, 47, 1882; (e) Lennox, J. C.; Murray, R. W. J. Electroanal. Chem., 1977, 78, 395; (f) Lenhard, J. R.; Murray, R. W. J. Electroanal. Chem., 1977, 78, 195.
37. (a) Fujihira, M.; Matsue, T.; Osa, T. Chem. Lett., 1976, 875; (b) Osa, T.; Fujihira, M. Nature, 1976, 264, 349; (c) Fujihira, M.; Tamura, A.; Osa, T. Chem. Lett., 1977, 361.
38. Wrighton, M. S.; Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G. J. Vac. Sci. Technol., 1978, 15, 1429.
39. (a) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. J. Am. Chem. Soc., 1978, 100, 1602; (b) Wrighton, M. S.; Bocarsly, A. B.; Bolts, J. M.; Bradley,



- M. G.; Fischer, A. B.; Lewis, N. S.; Palazzotto, M. C.; Walton, E. G.  
Adv. Chem. Ser., 1979, 101, 0000.
40. Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis,  
N. S.; Wrighton, M. S. J. Am. Chem. Soc., 1979, 101, 1378.
41. Fischer, A. B.; Wrighton, M. S.; Umaña, M.; Murray, R. W.  
J. Am. Chem. Soc., 1979, 101, 0000.
42. Bruce, J. A.; Wrighton, M. S. unpublished results.
43. Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas,  
O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. J. Electroanal. Chem.,  
1978, 87, 429.
44. Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.;  
Fischer, A. B.; Nadjo, L. J. Am. Chem. Soc., 1978, 100, 7264.
45. Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S.  
J. Electroanal. Chem., 1979, 100, 283.
46. Bocarsly, A. B.; Walton, E. G.; Wrighton, M. S. to be submitted.
47. Bookbinder, D.; Bocarsly, A. B.; Bradley, M. G.; Wrighton, M. S.  
to be submitted.
48. Schneemeyer, L. F.; Wrighton, M. S. to be submitted.
49. Bolts, J. M.; Wrighton, M. S. J. Am. Chem. Soc., 1979, 101, 0000.
50. Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S.  
J. Am. Chem. Soc., 1979, 101, 0000.

**Table I. Durable Photoanode Materials for Photoelectrolysis of Water.<sup>a</sup>**

Material	$E_{BG}$ , eV	Comments	Reference
TiO <sub>2</sub>	3.0	Rugged, but $E_{BG}$ too large and $E_{CB}$ and $E_{VB}$ too positive.	11,16
SrTiO <sub>3</sub>	3.2	Basis of most efficient cell for H <sub>2</sub> , O <sub>2</sub> production, $E_{BG}$ too large, $E_{VB}$ too positive.	13,16,17
SnO <sub>2</sub>	3.5	$E_{BG}$ too large; $E_{CB}$ and $E_{VB}$ too positive; produces H <sub>2</sub> O <sub>2</sub> in acidic media.	16,18a
KTaO <sub>3</sub>	3.4	$E_{BG}$ too large, $E_{VB}$ too positive.	18b
Fe <sub>2</sub> O <sub>3</sub>	-2.2	Relatively good visible response but $E_{VB}$ and $E_{CB}$ too positive.	19

<sup>a</sup>Many other "stable" photoanodes are known (see ref. 19); these are representative.

Table II. Non-Oxide Photoanodes Which Can Be "Stabilized" by Chalcogenide Ions.

Semiconductor	$E_{BG}$ , eV	References
CdS	2.4	} 21-25
CdSe	1.7	
CdTe	1.4	
GaP	2.2	24c
GaAs	1.4	24c, 25c, d
InP	1.3	24d
CuInS <sub>2</sub>	1.4	25e
Bi <sub>2</sub> S <sub>3</sub>	~1.4	23

**Table III.** Electrode Materials Derivatized by Hydrolytically Unstable Ferrocene Reagents, I, II, or III.

Electrode	Comments	References
Pt	{ Reversible, high coverages, very durable, $E^\circ$ within 100 mV of solution ferrocene, Auger and XPES of surface shows ferrocene polymer signals.	41-44
Au		
n-type Si	{ Durable, n-type behavior, (photooxidation, dark reduction) photoanodic peak as negative as $-0.1$ V vs. SCE, $-0.5$ V contra-thermodynamic.	39,40,45,46
n-type Ge	{ Lower output photovoltage than n-type Si; dark anodic currents observed due to surface states and/or low band gap (0.7 eV).	30
p-type Ge & Si	Not Fully Characterized	47
n-type MoS <sub>2</sub>	Not Fully Characterized	48
n-type GaAs	{ Similar to n-type Si, but more contrathermodynamic photo-oxidation routinely possible	49
n-type TiO <sub>2</sub>	{ Not fully characterized, but shows evidence for "surface states" located between $E_{CB}$ and $E_{VB}$ .	48

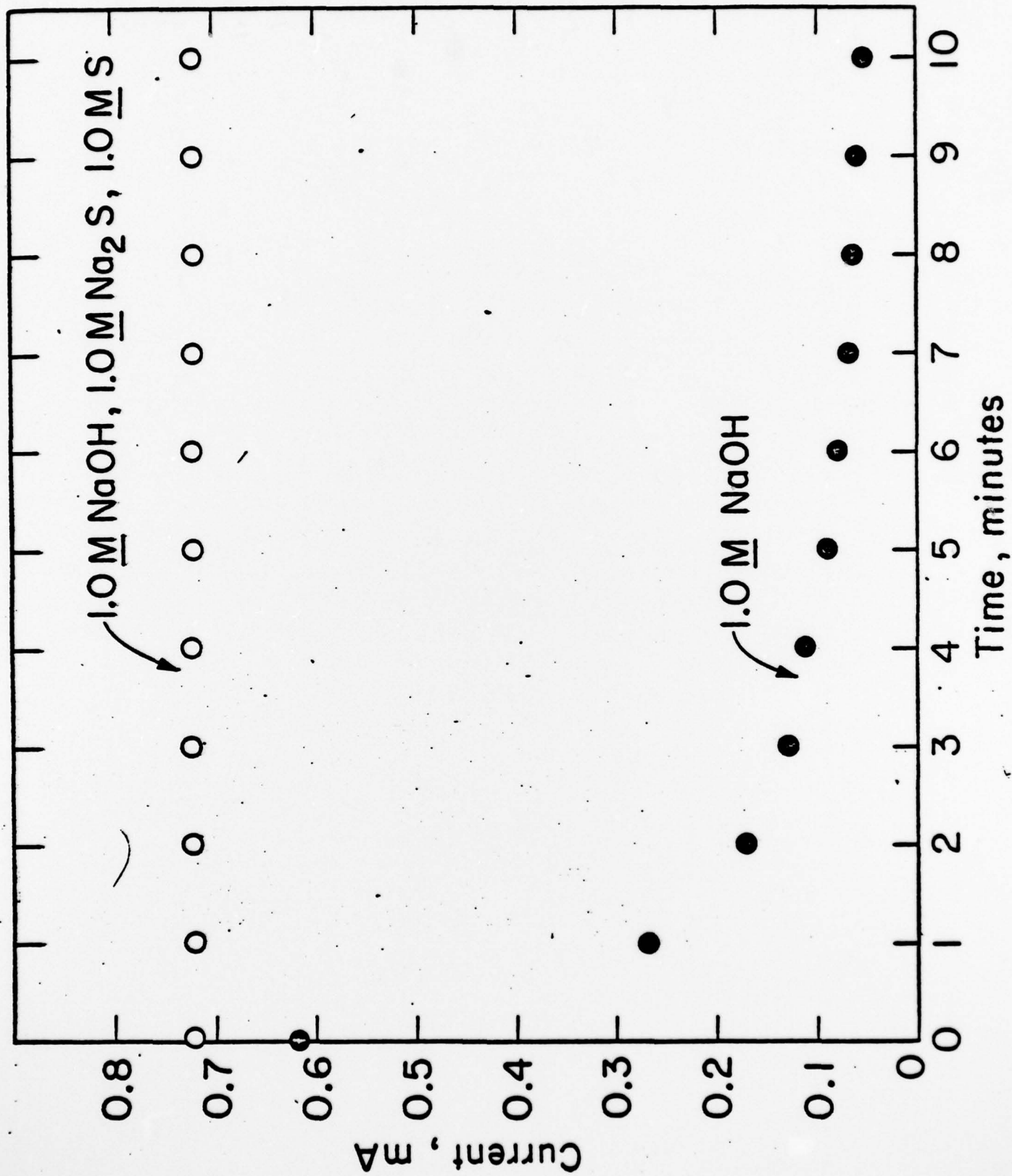


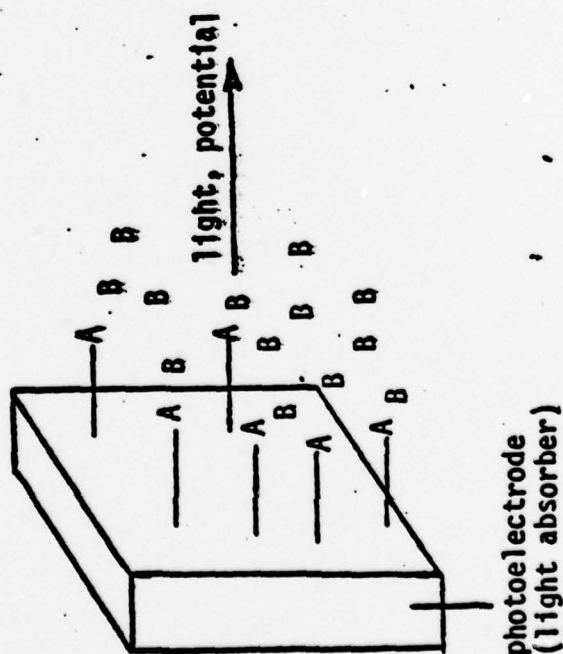
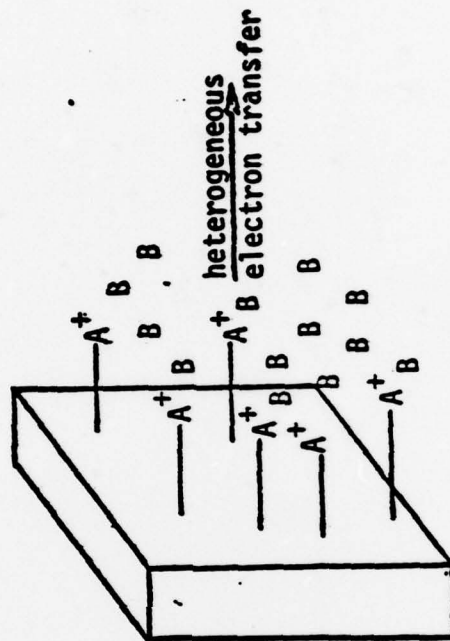
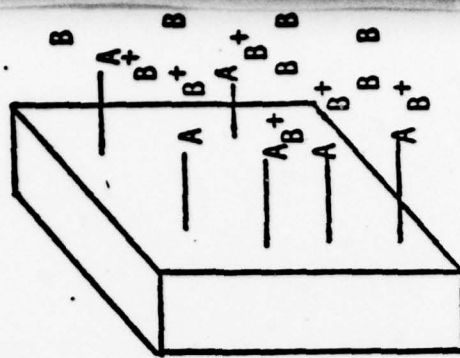
### Figure Captions

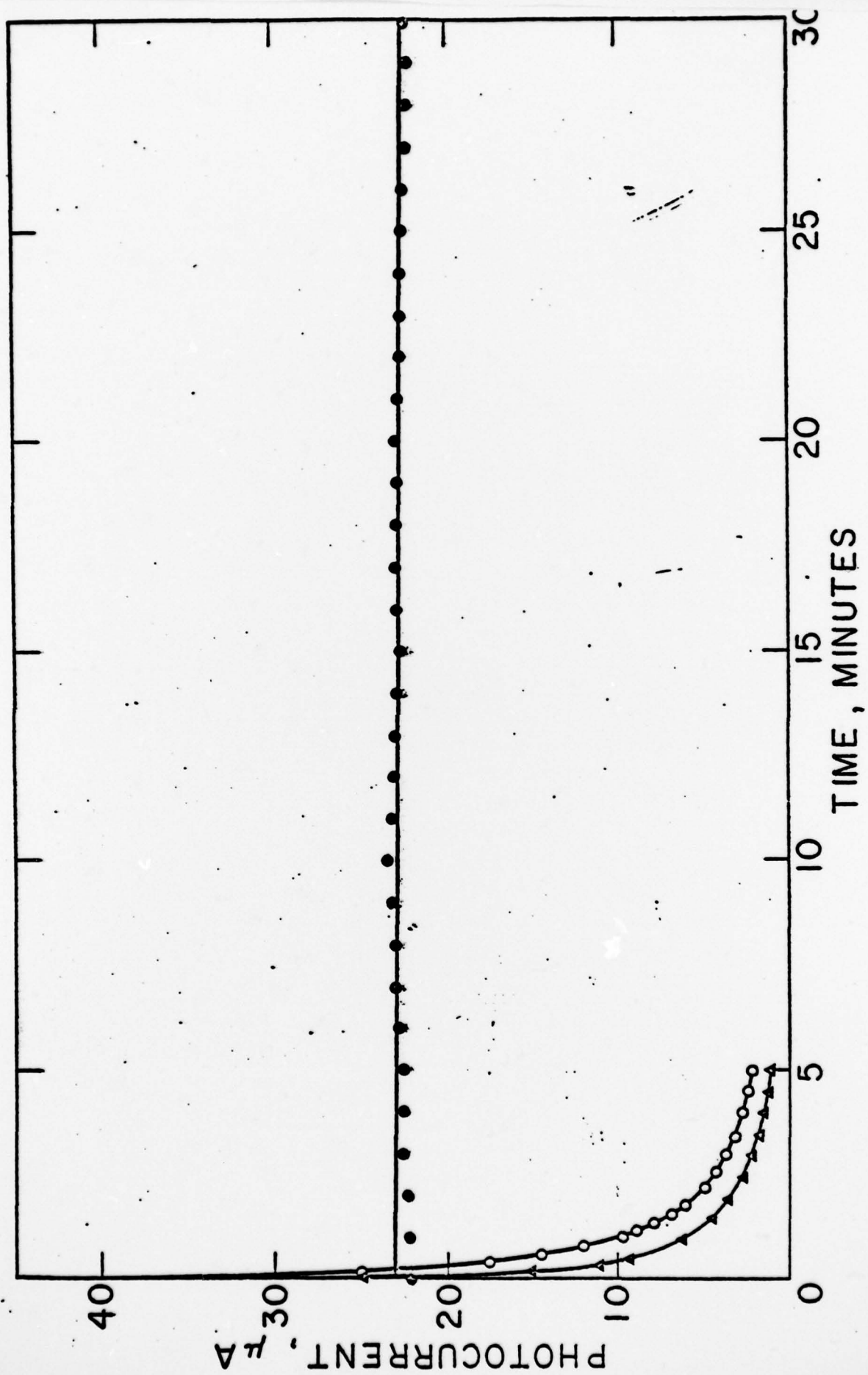
**Figure 1.** Photocurrent against time for 632.8 nm ( ~3 mW ) illumination of single crystal (0001 face exposed) n-type CdSe ( $E_{\text{GG}} = 1.7$  eV) photoanode in 1.0 M NaOH (●) and 1.0 M NaOH, 1.0 M  $\text{Na}_2\text{S}$ , 1.0 M  $\text{S}^{2-}$  (○) aqueous electrolytes with a Pt counterelectrode. The current in the  $\text{S}_n^{2-}$  electrolyte was continued an additional 48 h without variation. In the absence of  $\text{S}_n^{2-}$  photocurrent falls rapidly owing to photodegradation of surface. Reprinted with permission from Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc., 1976, 98, 6855.

**Figure 2.** Pictorial representation of mediated oxidation of solution species B where A is the electrode-attached electroactive species. Reprinted with permission from Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. J. Am. Chem. Soc., 1979, 101, 1378.

**Figure 3.** "Stabilization" of n-type Si in aqueous solution by derivatization. Plots of photocurrent against time for a single n-Si electrode illuminated with 632.8 nm light. Photoelectrode held at +0.2 V vs. SCE in stirred solutions. Supporting electrolyte is 0.1 M  $\text{NaClO}_4$  in doubly distilled deionized  $\text{H}_2\text{O}$ . Run 1 (Δ), HF-etched "naked" electrode in supporting electrolyte only. Run 2 (○), "naked" electrode re-etched with HF, in supporting electrolyte plus  $4 \times 10^{-3}$  M  $\text{Fe}(\text{CN})_6^{4-}$ . Run 3 (●), electrode derivatized with (1,1'-ferrocendiyl)dichlorosilane, II, in same solution as run 2. Reprinted with permission from Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. J. Am. Chem. Soc., 1979, 101, 1378.









For 359 - 696

472:GAN:716:tam  
78u472-608TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	

Encl 1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copie</u>
Dr. Paul Delahay New York University Department of Chemistry New York, New York 10003	1	Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1
Dr. R. A. Osteryoung Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1	Dr. P. J. Hendra University of Southampton Department of Chemistry Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Case Western Reserve University Department of Chemistry Cleveland, Ohio 44106	1	Dr. Sam Perone Purdue University Department of Chemistry West Lafayette, Indiana 47907	1
Dr. D. N. Bennion University of California Chemical Engineering Department Los Angeles, California 90024	1	Dr. Royce W. Murray University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus California Institute of Technology Department of Chemistry Pasadena, California 91125	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Technical Library	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. J. H. Ambrus The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	
Dr. Adam Heller Bell Telephone Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Oakland University Department of Chemistry Rochester, Michigan 48063	

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>	
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1	The Reliability Analysis Center RADC (RBRAC) Griffiss AFB, New York 13441
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	
<del>Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139</del>	<del>1</del>	
Larry E. Plew Naval Weapons Support Center Code 3073, Building 2906 Crane, Indiana 47522	1	
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California 92803	1	
Dr. M. G. Sceats University of Rochester Department of Chemistry Rochester, New York 14627	1	